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## Catalytic carbonylation of acrylic acid to succinic anhydride: en route to the synthesis of a bio-based monomer

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Nowadays, the share of plastics reaches 90 % of the production of petrochemicals, and the volumes of polymers produced is expected to keep growing in the coming years.<sup>1</sup> While fulfilling an increasing demand for these organic materials, it is necessary to improve their sustainability and replace the fossil feedstock used in their synthesis with renewable alternatives. In this context, we are targeting the formation of a monomer, succinic anhydride, from bio-based starting materials.

The current industrial production of succinic anhydride relies on the hydrogenation of maleic anhydride, which is itself produced from the oxidation of butane, a petrochemical.<sup>2</sup> An alternative route, currently explored at the laboratory scale, consists in promoting the catalytic carbonylation of another petrochemical, namely  $\beta$ -propiolactone.<sup>3</sup> In order to build a new synthetic pathway towards succinic anhydride, which would fit the challenges described above, we developed the carbonylation of an isomer of  $\beta$ -propiolactone, acrylic acid. Indeed, acrylic acid is not only a common platform chemical, but it can also be produced from the dehydration of lactic acid.<sup>4</sup>

Early studies on the carbonylation or hydroformylation of acrylic acid highlighted the difficulty of performing a selective, efficient and direct carbonylation reaction on acrylic acid.<sup>5</sup> Yet, by designing a selective low-valent cobalt complex supported by phosphine ligands, the production of acrylic acid to succinic anhydride was unlocked, thanks to mild reaction conditions (90 °C, 16 bar).<sup>6</sup> Screening of several reaction parameters such as gas phase pressure and composition, ligands and temperature, enabled us to propose some mechanistic hypotheses to rationalize the trends observed during this challenging carbonylative ring-closure.

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<sup>1</sup> Lange J.-P. Towards circular carbo-chemicals – the metamorphosis of petrochemicals. *Energy Environ. Sci.* **2021**, *14*, 4358-4376.

<sup>2</sup> Fumagalli C. Succinic acid and succinic anhydride. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley, 2000. Updated April 14, 2006.

<sup>3</sup> Nasr Allah T.; Ponsard L.; Nicolas E.; Cantat T. Catalytic challenges and strategies for the carbonylation of  $\sigma$ -bonds. *Green Chem.* **2021**, *23*, 723-739.

<sup>4</sup> Ohara T.; Sato T.; Shimizu N.; Prescher G.; Schwind H.; Weiberg O.; Marten K.; Greim H.; Shaffer T. D.; Nandi P. Acrylic Acid and Derivatives. In *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley, 2003. Updated January 3, 2020.

<sup>5</sup> a) Falbe J. Ring Closures with Carbon Monoxide. In *Carbon Monoxide in Organic Synthesis*; Springer, 1970; pp 147-174. b) Dessole, G.; Marchetti, M.; Taddei, M. Hydroformylation of Terminal Alkenes Supported on Solid Phase: Synthetic Tool for Combinatorial Chemistry. *J. Comb. Chem.* **2003**, *5*(3), 198-200.

<sup>6</sup> Pietraru M.-H.; Lentz N.; Ponsard L.; Nicolas E.; Cantat T. Patent submitted on November 12th, 2021, FR2111996.